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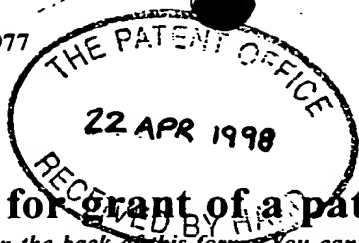
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Patent 275225-10 202047  
JPO/713- 23.00 - 1005507.1

# Request for grant of a patent

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1. Your reference HL58057/WS/VVT

2. Patent application number  
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3. Full name, address and postcode of the or of each applicant (*underline all surnames*)  
Hugh P. CRAIG  
29 Wallace Drive, Eaton Bray  
Dunstable, Beds. LU6 2DF

Patents ADP number (*if you know it*)  
If the applicant is a corporate body, give the country/state of its incorporation

074 22447 001.

4. Title of the invention  
Adhesive and Encapsulating Material with Fluxing Properties

5. Full name of your agent (*if you have one*)  
Haseltine Lake & Co.  
"Address for service" in the United Kingdom to which all correspondence should be sent (*including the postcode*)  
Imperial House  
15-19 Kingsway  
London WC2B 6UD

Patents ADP number (*if you know it*)

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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing ( <i>day/month/year</i> )

8. Is a statement of inventorship and of right to a grant of patent required in support of this request? (*Answer "Yes" if:*  
a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
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No

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Continuation sheets of this form

Description 9

Claim(s) 5

Abstract 1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

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Translations of priority documents

Statement of inventorship and right to a grant of patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application

Signature

Date

22nd April 1998

12. Name and daytime telephone number of person to contact in the United Kingdom

Mr W Silverman

[0171] 420 0500

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ADHESIVE AND ENCAPSULATING MATERIAL  
WITH FLUXING PROPERTIES

5           This invention relates to electrical  
interconnection methods in electronic circuitry and  
more particularly to flip chip attachment and  
encapsulation of both naked semi-conductors and chip  
scale packages (CSPs). The technology is commonly  
10           referred to as underfill technology.

          As is noted in US-A-5 128 746, solder bump  
interconnections when attaching chips to electronic  
circuitry eliminate the expense, performance  
limitations, low productivity and poor space  
15           utilisation of wire bonding. As circuit density  
increases occur, while circuit board and assembly sizes  
continue to shrink, so-called flip-chip interconnection  
using solder bumps has proved to be the most suitable  
technique for satisfying such demands.

20           With the most common form of flip-chip  
interconnection, solder bumps are placed on terminals  
of the integrated circuit being produced while the  
substrate for the integrated circuit is still in the  
form of a small wafer or die. Commonly, the eutectic  
25           Sn/Pb 60/40 or a high melting point alloy such as Sn/Pb  
3/97, which is known to have been employed in the IBM  
C4 process, is employed. The die or wafer carrying the  
integrated circuit is to be joined to a substrate and  
for this purpose the die or wafer will be inverted  
30           (hence the term flip-chip). For this purpose it is  
current manufacturing practice to place a flux or  
solder paste on the substrate. This material will  
adhere the die to the substrate for reflow. The  
assembly produced is subjected to a heat sufficient to  
35           melt or collapse (C4 process) the solder bump and form  
the required interconnections. The flux residue must

then be removed to prevent corrosion occurring to the die and, importantly, to allow free ingress of a subsequent underfill resin which is to encapsulate the various semi-conductors of the electronic circuitry produced.

For this latter purpose, an underfill encapsulant resin is applied around and under the die following reflow and flux removal. The very small gap between the die and substrate must be completely filled in order to provide environmental protection for the device. The filling of this gap is dependent on capillary action of the encapsulant material between the integrated circuit and substrate. The filling of the gap has proved to be a procedure which is very time consuming, expensive and difficult to achieve in the desired quality and is generally an unreliable procedure, particularly when a relatively large die is used. Moreover, the low viscosity of encapsulant material needed to ensure capillary action runs counter to the need to control thermal expansion and thermal conductivity by filling the encapsulation resin with ceramic powder which generally increases the viscosity of the resin. A solution to this problem has been to heat the substrate/component assembly to reduce initially the viscosity of the underfilling encapsulant resin. Temperatures must be precisely controlled and the process is difficult to control since the elevated temperature triggers the curing mechanism thus raising viscosity prematurely. For these various reasons, the underfilling process currently employed has low productivity and high space/equipment needs.

In the aforementioned US-A-5 128 746, it is proposed to add a fluxing agent to the encapsulant resin, the encapsulant resin being dispensed onto the substrate before the integrated circuit-carrying chip is placed in the encapsulant resin for reflow. US-A-5 128 746 discloses the use of strong organic

dicarboxylic acids as examples of commercially available fluxing agents. A fluxing encapsulant resin of such type has three very serious drawbacks which compromise the integrity of the interconnection.

5 Unreacted acid remains in the encapsulant after reflow and can and will attack any corrode metal present, especially on the die or wafer. This problem is exacerbated by the decreased environmental resistance of such adhesive composition due to the presence of  
10 unreacted resin. As the adhesive composition has relatively low resistance to humidity and moisture, the corrosion problem is thus intensified. Moreover, the addition of acids of the stated type to epoxy resin adhesives compromises the stability of the adhesive,  
15 greatly reducing pot life and making cure characteristics variable. This will have a major effect on reliability and process control.

It is an object of this invention to provide a thoroughly curable adhesive which does not suffer the  
20 problem of unreacted acid remaining in the encapsulant after reflow.

According to one aspect of the present invention there is provided a thermally curable adhesive composition which comprises:

- 25 (a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent;
- (b) a solid chemical crosslinking agent for said  
30 polymer, the crosslinking agent having fluxing properties and being unreactive with the polymer without catalyst; and
- (c) a latent catalyst for the crosslinking agent which is liberated on application of heat,  
35 which composition is thermally curable when heated to soldering temperatures, the cross-linking agent being

capable of reaction with said polymer or reactive monomer to block all potentially corrosive fluxing sites, which composition is storage and reaction stable until at a temperature at which components (b) and (c) cause cross-linking and curing of reactive monomer or polymer.

A crosslinking agent to be employed in the practice of the present invention will have fluxing properties so as to enable it to remove oxides from the material with which it is in contact, i.e. die and substrate metallisation, thereby allowing solder joint formation. The crosslinking agent is moreover capable of complete reaction with thermosetting polymer to neutralise, i.e. react with or block, effectively all potentially corrosive fluxing sites. The composition itself is storage and reaction stable until heated to a temperature at which the latent reaction catalyst effectively causes the crosslinking agent to cure the thermosetting polymer and at which temperature the crosslinking agent will have melted and dissolved in the polymer or monomer.

Thus, the present invention provides chip underfill and encapsulation adhesive compositions having fluxing properties which enable one to achieve overall a rugged structure with protection of integrated circuits which have been previously solder bumped and then flip chip connected to a substrate with a metallisation pattern. During reflow, the fluxing achieved with the crosslinking agent allows metallic interconnection to be achieved between solder bump and metallisation pads on the substrate. The adhesive composition then reacts and cures, fully neutralising all reactive fluxing sites to provide a fully adhered encapsulate underfill that is non-corrosive and environmentally resistant. The compositions are stable and provide a long storage life at ambient



temperatures, typically 20-25°C, while maintaining predictable processing characteristics. The adhesive compositions lack the substantial debilitating defects in the hitherto known compositions by providing a means for predepositing the underfill and eliminating separate fluxing and cleaning. The adhesive composition may be modified to optimise CTE, glass transition temperature (T<sub>g</sub>), elasticity modulus and thermal conductivity without detriment to the aforementioned benefits or detriment to the require rheological properties which allow for ease of deposition, for example by syringe dispensing. In addition, curing is achieved readily during any suitable thermal treatment, for example during reflow soldering. The underfill may only be partially cured after one or several solder reflow cycles, thus enabling ease of reworking of the device. Full cure is then achieved in a separate post-cure heat application. Alternatively, full cure may be obtained from one or two reflow cycles if reworkability is not required.

The invention thus also provides, in a second aspect, a method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition according to the first aspect of the invention being applied to one and/or both of said electrical component and said substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced from said monomer or polymer

in situ.

5       Insofar as the solder is concerned, this may  
consist of one or more metals which provide a suitable  
low melting point material. The metals employed are  
typically selected from tin, lead, bismuth, cadmium,  
10       zinc, gallium, indium, tellurium, mercury, thallium,  
antimony and selenium. The preferred such metal is tin  
or a tin/lead alloy. Specific examples of solders  
which may be employed are the aforementioned eutectic  
15       Sn/Pb 60/40 and the high melting point Sn/Pb 3/97.

      The thermosetting polymer or monomer utilised in  
the compositions of this invention is an adhesive  
substance which is preferably liquid at ambient  
temperature. Thus one may utilise a reactive polyester  
15       or an epoxide monomer or polymer such as an epoxy  
Novolak or epoxide precursor thereof. A preferred  
epoxy resin is either a diglycidyl ether of bisphenol A  
or a diglycidyl ether of bisphenol F. In preferred  
practice, such an epoxy resin is a B-stage resin or a  
20       resin which may be "B-staged" after application,  
thereby making it possible for there to be a delay  
before bringing together the component and the  
substrate. Other preferred epoxy materials to use are  
substances from the Araldite series of Ciba-Geigy  
25       Resins, such as the trifunctional epoxide MY10510 and  
the difunctional cycloaliphatic epoxide ERL 4221 which  
may be used singly or in admixture. The Araldite  
MY10510 may be replaced by Aradite MY19512, altetra  
functional epoxide. MY19512 may be used alone, too, as  
30       may the trifunctional epoxide MY10510. The composition  
of the invention may also contain a monomer precursor  
for a polymer, e.g. an epoxide compound when an epoxy  
resin is required.

35       The crosslinking agent with fluxing properties is  
preferably a di- or polycarboxyl compound which is solid  
at ambient temperature and insoluble in the monomer or

polymer until heated, in practice generally to  
soldering temperatures, and such cross linking agents  
are generally referred to hereafter as polyacids. Such  
polyacids serve as a fluxing agent for the oxide  
5 material present on the solder, which metal oxide is a  
catalyst for reaction between an epoxy resin and the  
carboxyl groups of the polymer at elevated  
temperatures. Such polyacid may be in particular a  
carboxylated polymer, a polymer fatty acid, such as a  
10 dimerised or trimerised fatty acid, or a long chain ( $C_8$   
or greater, preferably  $C_{10}$  or greater) polycarboxylic  
acid, preferably dicarboxylic acid. An organic trimer  
fatty acid having a functionality greater than 1  
provides more than one reaction site, with an epoxy  
15 resin then serving to create a macromolecule that  
provides adhesive. The aforementioned preferred  
carboxyl-containing polymers also provide multiple  
reaction sites. A particularly preferred example of a  
polymer containing two or more carboxyl groups which  
20 may be employed is a styrene-acrylic acid copolymer. A  
preferred dicarboxylic acid is dodecanedioic acid.

Other crosslinking agents with fluxing properties  
which can be used are mono di-and polyhydrazides which  
are solid at ambient temperature and insoluble in the  
25 monomer or polymer until heated, in practice generally  
to soldering temperature. A preferred such compound is  
adipic dihydrazide. Because of the differing  
reactivities of polycarboxylic acids and hydrazides, it  
is preferred to use a mixture of crosslinking agents,  
30 such as dodecanedioic acid and adipic dihydrazide, the  
higher reactivity of the latter being countered by the  
lower reactivity of the former.

While the oxide removed from the solder as a  
result of the fluxing activity of the crosslinking  
35 agent may act as a catalyst for the curing of the  
polymer, curing in the manner of a snap cure fix is

achieved when an imidazole only is present as catalyst active at the elevated temperature utilised for soldering. A preferred such compound is phenyl imidazole. Other latent reaction catalysts which can be used are tertiary amines with the amine groups optionally substituting the reactive monomer or polymer, as in the aforesaid Araldite MY10510 or MY19512, or metallic salts such as tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

The use in adhesive compositions employed for encapsulating flip chip connections of ceramic powders to enhance thermal expansion and modulus properties of the composition has already been mentioned herein and is preferably to be adopted in the practice of the present invention. It is preferred that such ceramic powders be highly thermally conductive to enhance the connection between solder bump and conductor on the substrate while ensuring that the compositions retain the low viscosity necessary for fluxing and for ease of deposition. The filler is preferably a nominally  $25\mu$  diameter spherical ceramic bead or hollow sphere composition. More generally, it maybe a glass or ceramic powder comprising spherical particles of  $5-75\mu$  diameter or comprise essentially monodisperse spherical particles having a single diameter of  $5-75\mu$ . The ceramic powder has preferably a very high thermal conductivity. Examples of such ceramic powders which may be employed are  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2/\text{ZnO}$ , barium sulphate and diamond dust. In some cases, it is preferred that the ceramic powder utilised has instead a very low or negative coefficient of thermal expansion, too, and if this requirement is imposed on the ceramic powder then a preferred example is aluminium lithium silicate.

When utilising the compositions of the invention,

there is no need for them to be introduced subsequent to formation of a solder connection with the attendant difficulties identified above. It is possible for the composition to be predeposited, before emplacement and soldering of electronic component to substrate, on either or both of the electronic component and the substrate. As there is no need for a separate fluxing agent to be employed, the presence of the composition on one or other of the electronic component and the substrate fulfils the required fluxing function.

Insofar as the composition may be applied to the electronic component, then this may be to the die overall whether it is in wafer form or as separate discrete devices. Application of the composition may be by screen printing, stencil printing, dispensing, spinning or any other known method for applying a composition to discrete areas.

The ease of working in accordance with the method of this invention enables the composition to contain the thermosetting resin in the form of a B-stageable precursor for application to die, substrate or carrier tape and then B-staging so as to form a handleable film which becomes fully crosslinked only when the soldering operation is carried out.

CLAIMS

1. A thermally curable adhesive composition which comprises:

5

(a) a thermosetting polymer, or a monomer which is polymerisable to yield a thermosetting polymer, said polymer being crosslinkable when subject to the action of a chemical crosslinking agent;

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(b) a solid chemical crosslinking agent for said polymer, the crosslinking agent having fluxing properties and being unreactive with the polymer without catalyst; and

15

(c) a latent catalyst for the crosslinking agent which is liberated on application of heat, which composition is thermally curable when heated to soldering temperatures, the cross-linking agent being capable of reaction with said polymer or reactive monomer to block all potentially corrosive fluxing sites, which composition is storage and reaction stable until at a temperature at which components (b) and (c) cause cross-linking and curing of reactive monomer or polymer.

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2. A composition according to claim 1, wherein said chemical crosslinking agent is selected from polyacids and hydrazides which are solid at ambient temperature and insoluble in the monomer or polymer until heated to soldering temperature.

30

3. A composition according to claim 2, wherein the polyacid is selected from dimerised and trimerised fatty acids, polymers containing two or more carboxyl groups and di- and polycarboxylic acids.

35

4. A composition according to claim 3, wherein the polycarboxylic acid is a C<sub>8</sub> or greater dicarboxylic acid.

5. A composition according to claim 2, wherein the hydrazide is a monohydrazide, dihydrazide or polyfunctional hydrazide.

5 6. A composition according to any one of claims 2 to 5, wherein the crosslinking agent contains a dihydrazide and/or a dicarboxylic acid.

10 7. A composition according to claim 6, wherein the crosslinking agent contains adipic dihydrazide and/or dodecanedioic acid.

8 8. A composition according to claim 3, wherein the crosslinking agent is a styrene acrylic acid copolymer.

15 9. A composition according to any preceding claim, wherein said polymerisable monomer is an epoxide.

20 10. A composition according to any one of claims 1-8, wherein said polymer is an epoxy resin.

11. A composition according to claim 10, wherein said polymer is a B-staged epoxy resin.

25 12. A composition according to claim 11, wherein the said polymer is a diglycidyl ether of bisphenol A.

30 13. A composition according to claim 9, wherein the said resin is a tri- or tetrafunctional epoxide or a difunctional cycloaliphatic epoxide or a mixture of two or more such epoxides.

14. A composition according to any preceding claim, wherein the latent reaction catalyst is selected from tertiary amines, imidazoles and metallic salts.

5 15. A composition according to claim 14, wherein the imidazole is phenyl imidazole.

10 16. A composition according to claim 14, wherein the tertiary amine is constituted by self catalysing tertiary amines groups substituting the reactive monomer or polymer.

15 17. A composition according to claim 16, wherein the reactive monomer is a tertiary-amine substituted trifunctional or tetrafunctional epoxide.

20 18. A composition according to claim 14, wherein the metallic salt is tin octanoate, dibutyl tin dilaurate, ferric acetylacetonate, and cobalt (III) acetylacetonate.

19. A composition according to any preceding claim which further comprises a thermally resistant filler.

25 20. A composition according to claim 18, wherein said filler reduces thermal expansion of the composition while not effecting substantially the viscosity thereof.

30 21. A composition according to claims 19 and 20, wherein the filler is constituted by nominally  $25\mu$  spherical ceramic beads or hollow spheres.

35 22. A composition according to claim 19, wherein the filler is a ceramic or glass ceramic powder comprising spherical particles with diameters in the range from 5-



75 $\mu$ .

23. A composition according to claim 19, wherein the filler is a ceramic or glass ceramic powder consisting essentially of monodisperse spherical particles having a single diameter in the range from 5-75 $\mu$ .

24. A composition according to claim 19, wherein the filler is a thermally conductive ceramic powder.

25. A composition according to claim 24, wherein the ceramic powder is selected from SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> /ZnO, barium sulphate and diamond dust.

26. A composition according to claim 19, wherein the ceramic powder has a low or negative coefficient of thermal expansion.

27. A composition according to claim 26, wherein the ceramic material is aluminium lithium silicate.

28. A method of producing an electronic device which comprises opposing an electrical component having a plurality of electrical terminations, each termination including a solder bump, and a component-carrying substrate having a plurality of electrical terminations corresponding to the terminations of the electrical component, with a thermally curable adhesive composition according to any one of claims 1 to 27 being applied to one and/or both of said electrical component and said substrate, bringing the electrical component and substrate into contact at elevated temperature and thereby soldering the electrical component to the substrate and simultaneously achieving encapsulation thereof in thermoset polymer produced from said monomer or polymer in situ.

29. A method as claimed in claim 28, wherein the thermally curable adhesive composition is applied to one and/or both of the said electrical component and said substrate prior to bringing the two together.

5

30. A method as claimed in claim 28 or 29, wherein no fluxing agent is applied to either said electrical component or said substrate prior to application of the solder curable adhesive composition.

10

31. A method as claimed in any one of claims 28 to 30, wherein the thermally curable adhesive composition is applied to a die, either in wafer form or as separate discrete devices.

15

32. A method as claimed in any one of claims 28 to 31, wherein the thermally curable adhesive composition is applied by screen printing, stencil printing, dispensing or spinning.

20

33. A method as claimed in any one of claims 28 to 32, wherein the thermally curable adhesive composition is applied in B-stageable form and B-staged in situ.

ABSTRACT

ADHESIVE AND ENCAPSULATING MATERIAL  
WITH FLUXING PROPERTIES

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An adhesive material which comprises a thermosetting polymer, or monomer precursor, the polymer being crosslinkable under the reaction of a chemical crosslinking agent, a solid chemical crosslinking agent for the polymer which has fluxing properties and is unreacted with the polymer without a catalyst and a latent catalyst for the crosslinking agent which is liberated on application of heat, is employed on a substrate having a metallisation pattern or a solder bumped electrical component which are brought together in a procedure involving reflow followed by heating for soldering of the component to the substrate during which the latent catalyst is liberated and soldering takes place with simultaneous encapsulation of the component in cured polymer.

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22nd April 99

Haseltine Lake & Co

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